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## (54) MANUFACTURE OF CALCIUM SULPHATE

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London, SW1 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the manufacture of calcium sulphate.

Calcium sulphate alpha-hemihydrate may be manufactured by interacting a source of calcium ions and a source of sulphate ions in an aqueous system at a temperature which is above the calcium sulphate hemihydrate/calcium sulphate dihydrate transition temperature apertaining under the reaction conditions, followed by separating the alpha-hemihydrate as a moist solid and then drying. Alternatively, the calcium ions and sulphate ions may be reacted below the aforesaid transition temperature to form gypsum, which is separated as a moist solid, and either decomposed directly to give the alpha-hemihydrate, or the moist solid is slurried with water and decomposed to the alpha-hemihydrate in an autoclave.

In the aforesaid processes, it is convenient to use calcium chloride as a source of calcium ions and sulphuric acid as a source of sulphate ions. We have now found that the source of calcium ions may conveniently be calcium carbonate in the form of "brine mud" which is an aqueous slurry containing calcium carbonate and magnesium hydroxide produced in brine purification processes, for example in the preparation of purified brine for use in the ammonia soda process and in the production of electrolytic chlorine, and in the preparation of purified salt.

According to the present invention we provide a process for the manufacture of a calcium sulphate which comprises

- (i) interacting "brine mud" with sulphuric acid to produce a slurry comprising calcium sulphate in the solid phase and gaseous carbon dioxide.
- (ii) separating moist calcium sulphate from the slurry produced in stage (i), and

- (iii) heating the moist calcium sulphate from stage (ii) to give a dry calcium sulphate.

Typically, "brine mud" containing calcium carbonate and magnesium hydroxide is obtained when purifying natural sodium chloride brine by the addition of sodium carbonate and sodium hydroxide or lime to precipitate calcium and magnesium impurities. It is produced in large quantities (of the order of 3000 tons/day) in the course of purifying natural sodium chloride brine for use in the ammonia soda process and in the production of electrolytic chlorine.

A typical analysis of the "brine mud" is as follows:—

	% by weight
CaCO <sub>3</sub>	8.75
Mg(OH) <sub>2</sub>	1.77
SrCO <sub>3</sub>	0.02
NaCl	21.80
Water	67.66

The carbon dioxide produced in stage (i) is conveniently used for the carbonation of an aqueous solution of sodium hydroxide, to give sodium carbonate. It is especially preferred to use this carbon dioxide to carbonate the caustic cell liquor produced in a diaphragm cell for the manufacture of chlorine from sodium chloride brine.

A range of aqueous solutions of sulphuric acid containing up to 98% by weight of H<sub>2</sub>SO<sub>4</sub> may be used in stage (i), and also fuming sulphuric acid or oleum, but it is preferred to use sulphuric acid solutions containing from 40% to 98% by weight of H<sub>2</sub>SO<sub>4</sub>. It is especially convenient to use impure sulphuric acid effluents which are produced in a number of industrial processes, for example the waste sulphuric acid produced in the manufacture of nitrobenzene, methyl methacrylate, and sodium cyanide, and the waste sulphuric acid obtained after being used as a drying agent (e.g. for drying chlorine gases, or chloromethanes).

The calcium sulphate solid phase obtained in stage (i) may be calcium sulphate alpha-hemihydrate, calcium sulphate dihydrate (gyp-

sum), or anhydrous calcium sulphate (anhydrite) dependent on the conditions of the reaction.

In an aqueous system containing no other ions than calcium ions and sulphate ions, the calcium sulphate hemihydrate/gypsum transition temperature in the reaction mixture is about 95°C. The transition temperature is effected, however, to some extent by the actual concentrations of the calcium ions and the sulphate ions and to a much greater extent by the concentrations of other ions which may be present in the reaction mixture, especially chloride ions. In the presence of chloride ions, the transition temperature is lowered. For example when reacting the "brine mud" with sulphuric acid in stage (i), the transition temperature is reduced to about 70°C in a reaction mixture containing a chloride concentration of 98 g/litre.

When it is desired to precipitate alpha-hemihydrate in stage (i), the reaction may be carried out at any temperature above the hemihydrate/gypsum transition temperature in the particular reaction mixture, but the degree of conversion of the reacting materials to alpha-hemihydrate increases with increase in temperature and increase in residence time. The process is preferably carried out at a temperature of at least 20 degrees centigrade above the transition temperature. The process may conveniently be carried out at 95 to 110°C at atmospheric pressure, or preferably at a temperature of at least 140°C, for example 150 to 160°C, at a super-atmospheric pressure (for example between 5 and 10 atmospheres absolute). The residence time is conveniently in the range 0.5 minute to 60 minutes, and preferably in the range 5 minutes to 15 minutes.

Stage (i) may be carried out in the presence of crystal habit modifiers which are known to assist in the production of alpha-hemihydrate of commercially useful crystalline structure, for example when producing alpha-hemihydrate from gypsum as described in U.K. 1,051,849. The habit modifiers include, for example, inorganic salts of trivalent metal ions, such as iron, aluminium, chromium, and polar organic compounds, for example acids and salts of acids.

When it is desired to precipitate gypsum in stage (i), the reaction may be carried out at any temperature below the hemihydrate/gypsum transition temperature in the particular reaction mixture (about 70°C–95°C). This stage of the process is conveniently carried out at atmospheric pressure. The residence time is conveniently in the range 0.5 to 60 minutes, and preferably in the range 2 to 10 minutes.

When it is desired to precipitate anhydrite in stage (i), the reaction may be carried out at any temperature above the anhydrite/gyp-

sum transition temperature in the particular reaction mixture (about 15–40°C), and in the presence of seed crystals of anhydrite.

The calcium sulphate solid phase may be separated from the slurry of calcium sulphate and liquor (comprising essentially water or dilute sodium chloride brine) by any convenient means, for example by filtration or centrifuging, provided the temperature of the separating stage is maintained at a temperature at which the particular calcium sulphate solid phase is stable. When separating alpha-hemihydrate, the filter or centrifuge is conveniently operated at 100°C; when separating gypsum, the filter or centrifuge is conveniently operated at ambient temperature. When separating anhydrite, the temperature is preferably below the temperature at which the anhydrite is precipitated.

The separated calcium sulphate solids are suitably washed with water and the combined washings and filtrate (which are essentially neutral but may contain small amounts of calcium, magnesium, chloride and sulphate ions) are discarded.

The separated calcium sulphate is heated to remove moisture and dry it, for example in a steam heated drier at 100 to 120°C, to give dry alpha-hemihydrate, gypsum or anhydrite.

The gypsum may, if desired, be converted to alpha-hemihydrate, for example by heating with steam in an autoclave reactor, preferably at a temperature of at least 140°C, for example 140°C to 160°C, and at a super-atmospheric pressure of at least 5 to 10 atmospheres absolute.

The process according to the present invention may be carried out batchwise, if desired, but it is especially applicable to continuous production.

The dried alpha-hemihydrate produced in the present process may be used without further modification in the manufacture of plasterboard, wall blocks or as an inert filler. The gypsum or anhydrite may be used, for example, as a filler in various industries such as cement, paper and glass. The present process also provides useful outlets for "brine mud" and for low grade sulphuric acids produced in a number of processes. The utilisation of such waste products reduces the environmental problems associated with their disposal.

The invention is illustrated by the accompanying drawing which shows a flow diagram relating to the production of calcium sulphate alpha-hemihydrate. "Brine mud" is fed to the stirred reactor 1 where it is reacted with waste sulphuric acid (typically containing 40% to 98%  $H_2SO_4$ ) at about 100°C. The carbon dioxide liberated in reactor 1 may conveniently be used to carbonate diaphragm caustic cell liquor to produce sodium carbonate.

The slurry of calcium sulphate alpha-hemi-

70

75

80

85

90

95

100

105

110

115

120

125

130

hydrate produced in reactor 1 is fed to a filter or centrifuge 2 operating at about 100°C.

5 The alpha-hemihydrate separated in the filter or centrifuge 2 is washed with water and the moist solid is passed to a steam heated drier 3 operating at about 120°C. Residual heat in the steam used in the drier 3 may be utilised by feeding the steam to the reactor 1.

10 The filtrate and washings recovered from the centrifuge 2 are discarded.

The invention is further illustrated but not limited by the following Example.

#### Example

15 53 ml of 98% sulphuric acid were added over a period of 15 minutes to 1 litre of "brine mud". The temperature of the "brine mud" containing approximately 95 g calcium carbonate and 22 g of magnesium hydroxide) was initially 102°C and the temperature of the reaction mixture fell to 98°C during the addition of the sulphuric acid. The reaction mixture was stirred for a further 25 minutes and then filtered under reduced pressure. The calcium sulphate solids were washed with water and then dried to give 30 129.5 g of calcium sulphate alpha-hemihydrate containing a small amount of unreacted calcium carbonate.

#### WHAT WE CLAIM IS:—

1. A process for the manufacture of a calcium sulphate which comprises

- 35 (i) interacting "brine mud" with sulphuric acid to produce a slurry comprising calcium sulphate in the solid phase and gaseous carbon dioxide.  
(ii) separating moist calcium sulphate from the slurry produced in stage (i), and  
40 (iii) heating the moist calcium sulphate from stage (ii) to give a dry calcium sulphate.

2. A process as claimed in Claim 1 wherein the sulphuric acid contains 40 to 98%  $H_2SO_4$ .

3. A process as claimed in Claim 1 or Claim 2 wherein the sulphuric acid is an impure sulphuric acid effluent.

50 4. A process as claimed in any one of the preceding claims wherein the reaction is carried out at a temperature which is above the calcium sulphate hemihydrate/calcium sulphate dihydrate (gypsum) transition temperature in the particular reaction mixture so as to produce calcium sulphate alpha-hemihydrate as the solid phase.

5. A process as claimed in claim 4 wherein the reaction is carried out at a temperature of at least 20 degrees centigrade above the hemihydrate/gypsum transition temperature. 60

6. A process as claimed in Claim 5 wherein the reaction is carried out in the range 95°C to 110°C at atmospheric pressure.

7. A process as claimed in Claim 5 wherein the reaction is carried out at 140°C to 160°C at superatmospheric pressure. 65

8. A process as claimed in Claim 7 wherein the reaction is carried out at 5—10 atmospheres absolute. 70

9. A process as claimed in any one of Claims 1—3 wherein the reaction is carried out at a temperature which is below the calcium sulphate hemihydrate/calcium sulphate dihydrate (gypsum) transition temperature in the particular reaction mixture so as to produce calcium sulphate dihydrate (gypsum) as the solid phase. 75

10. A process as claimed in any one of Claims 1—3 wherein the reaction is carried out at a temperature which is above the anhydrous calcium sulphate (anhydrite)/calcium sulphate dihydrate (gypsum) transition temperature in the particular reaction mixture and in the presence of said crystals of anhydrous calcium sulphate so as to produce anhydrous calcium sulphate (anhydrite) as the solid phase. 80

11. A process for the manufacture of calcium sulphate alpha-hemihydrate substantially as described herein with reference to and as illustrated in the drawing. 85

12. A process for the manufacture of calcium sulphate alpha-hemihydrate substantially as described in the Example. 90

13. Calcium sulphate alpha-hemihydrate whenever made by the process claimed in any one of Claims 1—8, 11 and 12.

14. Calcium sulphate dihydrate (gypsum) whenever made by the process claimed in any one of Claims 1—3 and Claim 9. 100

15. Anhydrous calcium sulphate (anhydrite) whenever made by the process claimed in any one of Claims 1—3 and Claim 10.

16. Carbon dioxide whenever made by the process as claimed in any one of the preceding claims. 105

17. Sodium carbonate whenever made by carbonating an aqueous solution of sodium hydroxide using the carbon dioxide made as claimed in claim 16. 110

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